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ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: **OLEFIN POLYMERS WITH STABILISERS AND POLYOLEFIN FIBRES PRODUCED THEREFROM**

(57) Abstract: An olefin polymer composition comprising (ppm with respect to the polymer): a lactone of the furan-2-one type, a phenol in amounts of 50 to 200 ppm, a sterically hindered amine in amounts of 50 to 300 ppm, and an organic phosphite and/or organic phosphonite in amounts of 50 to less than 280 ppm. The polymer composition contains the unsubstituted furan-2-one moiety in amounts ranging from 11 to 49 ppm with respect to the polymer. Staple fibres with high tenacity and elongation at break and non-woven fabrics are prepared from such an olefin polymer composition.

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“Olefin Polymers with Stabilisers and Polyolefin Fibres Produced Therefrom”

The present invention relates to thermoplastic polymers comprising a stabiliser mixture, fibres with improved bonding properties, thermal bonded non-woven fabric made from fibres produced from said polymers and a process for the preparation of said fibres. In particular, the invention relates to a polyolefin-based thermoplastic resin comprising a stabiliser mixture comprising at least one compound of the benzofuran-2-one type and a phenolic long-term stabiliser and thermal bondable fibres made up of such a stabilised polyolefin-based thermoplastic resin.

The definition of “fibres” also includes products similar to fibres, such as fibrils and cut filaments (staple fibres).

Fibres of certain thermoplastic materials are used widely in the manufacturing of thermally bonded products, such as non-woven fabrics, by various processes. Said processes are mainly staple carding/calendering, and any combination of them for composite structures of non-woven fabrics.

Thermal bonding staple by long and short spinning with carding/calendering is one of the main technologies applied to produce hygiene non-woven fabrics.

A fundamental requirement of polyolefin fibres for thermally bonded non-woven fabrics is that fibres bond to each other by means of the joint action of temperature and pressure on which the hot calendering process is based.

It is well known that additives to polymers have an effect on the bonding properties of the fibre and thus the mechanical properties of the non-woven fabric. Better bonding properties of the fibres lead to improved mechanical properties, in particular mechanical strength essentially defined by the bonding index, of the non-woven fabric.

Poor mechanical properties can sometimes be the consequence of remarkable oxidative degradation of the polymer as evidenced by increasing of melt flow rate.

It also well known that fibres obtained by polymers containing the most commonly used stabilisers have little welding capability. Therefore, the mechanical properties of non-woven textiles obtained by calendering the above-mentioned fibres are poor.

Hence, there is a need for the production of thermal bondable fibres that are not affected by the said drawback.

It is known in the prior art from international patent WO 02/31038 that blends of a secondary aromatic amine, sterically hindered phenol and a lactone chosen from the class of

2-phenylbenzofuran-2-one impart good stability against oxidative degradation to polymers as evidenced by retention of melt flow rate. The stabilisation of polymer with the disclosed blend requires a quite high amount of sterically hindered phenols, at least 450 ppm, according to the working examples.

Polyolefin fibres stabilised with stabiliser mixtures containing a lactone of the benzofuran-2-one type are already well known. Such stabiliser mixtures are phenol-free. For example, US patent No. 6521681 discloses a stabiliser mixture comprising (i) a lactone of the benzofuran-2-one type and (ii) a sterically hindered amine. Such stabiliser mixture can further comprising a third component, namely (iii) an organic phosphonite or phosphite.

US patent No. 5834541 discloses a stabiliser olefin polymer suitable for fibres. The olefin polymer is stabilised with a stabilised system comprising a phosphite and a benzofuranone and/or an N,N-dialkylhydroxylamine.

European Patent 1260618 discloses staple fibres made from propylene polymer comprising a lactone chosen from the class of 2-phenylbenzofuran-2-one and, optionally, phosphite or phosphonite.

Such stabiliser mixtures for polyolefin fibres do not satisfy in every respect the requirements that the fibre is required to meet. The use of such stabiliser mixtures leads to fibres with poor mechanical properties, especially low tenacity and elongation at break.

A polymer with poor mechanical properties also affects the spinning behaviour; in fact breakage of several filaments occurs during spinning process.

Unexpectedly, it has now been found thermoplastic polyolefins that do not exhibit the above-mentioned drawbacks thanks to stabilisers that form mixtures with a synergistic effect. The stabilised polymer according to the present invention achieves a good level of stabilisation in the extruder (melt stabilizer) and a controlled level of oxidative degradation just outside the spinneret (long term thermal ageing) leading to a moderate increasing of the value of the melt flow rate. Hence, the fibres and non-woven fabric according to the present invention also exhibit good mechanical properties, in particular high tenacity and elongation at break.

Surprisingly, fibres produced with the stabilised polymer according to the present invention also possess high thermoweldability and bonding properties.

The great advantage of the polymer as stabilised according to the present invention is that the increase in thermoweldability of the fibres is not to the detriment of the mechanical

properties to the fibre and, consequently, the non-woven fabric prepared therefrom.

The stabiliser polymer according to the present invention also improves the feasibility of the spinning process by reducing breakage of filaments during the spinning process.

The polymer composition and fibres according to the present invention exhibit no colouration although they contain a phenolic antioxidant because such antioxidant is present in small amounts. No colour change is an important requirement for certain applications, such as hygienic ones.

The present invention accordingly relates to an olefin polymer composition comprising (ppm with respect to the polymer):

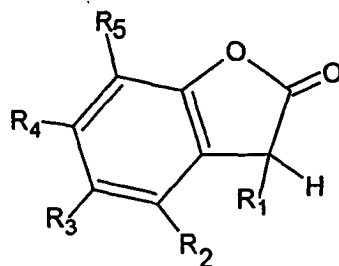
- a lactone of the furan-2-one type,
- a phenol in amounts of 50 to 200 ppm,
- a sterically hindered amine in amounts of 50 to 300 ppm, and
- an organic phosphite and/or organic phophonite in amounts of 50 to less than 280 ppm.

The polymer composition contains the unsubstituted furan-2-one moiety in amounts ranging from 11 to 49 ppm with respect to the polymer.

Preferably, the polymer composition contains 40 to 220 ppm, more preferably 50 to 200 ppm, of lactone of the furan-2-one type.

In one preferred embodiment of the invention, the lactone is of benzofuran-2-one type. Suitable benzofuran-2-ones and processes for making them are described in U.S. 4,325,863, 4,338,224, 5,175,312 and 5,344,860. The said compounds have already been applied in stabilising compositions or polyolefins as e.g. described in GB 2322374.

Examples of such benzofuran-2-ones are compounds of formula (I)

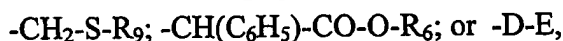
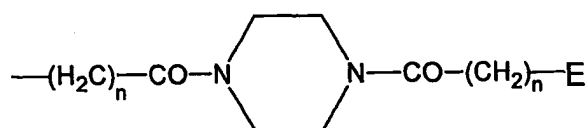
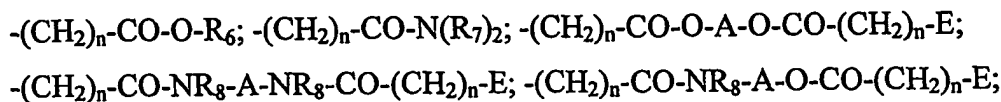


in which R_1 radical is any kind of substituent other than H, preferably non-substituted phenyl or substituted phenyl radicals; and R_2 to R_5 radicals independently are H or any kind of other substituents, preferably alkyl radicals.

Preferably, the substituents bonded to the phenyl group are 1 to 3 alkyl radical(s) from 1 to 12 carbon atom(s), more preferably C_1 - C_4 alkyl radical, and together having at most 18

carbon atoms, alkoxy radical(s) having 1 to 12 carbon atom(s), alkoxycarbonyl radical(s) having 2 to 18 carbon atoms or a halogen atom, such as chlorine.

Preferably R_2 is a radical of hydrogen, R_4 is a radical of hydrogen, linear or branched alkyl, having 1 to 12 carbon atoms(s), a C_4 - C_8 cycloalkyl, such as cyclopentyl, cyclohexyl, or a halogen atom, such as chlorine; R_3 radical has a meaning of R_2 or R_4 radical or is a radical of the formula



in which R_6 is a radical of hydrogen, linear or branched alkyl having 1 to 18 carbon atom(s), alkyl having 2 to 18 carbon atoms which is interrupted by oxygen or sulfur, dialkylaminoalkyl having a total of 3 to 16 carbon atoms, a C_4 - C_8 cycloalkyl, such as cyclopentyl, cyclohexyl, phenyl or phenyl which is substituted by 1 to 3 alkyl radicals together having at most 18 carbon atoms;

n is 0, 1 or 2;

the substituents R_7 , independently of one another, are a radical of hydrogen, linear or branched alkyl having 1 to 18 carbon atom(s), a C_4 - C_8 cycloalkyl, such as cyclopentyl, cyclohexyl, phenyl, phenyl which is substituted by 1 or 2 alkyl radicals together having at most 16 carbon atoms, a radical of the formula:



or together with the nitrogen atom to which they are attached form a piperidine or morpholine radical;

m is 1 to 18;

R_{10} is a radical of hydrogen, linear or branched alkyl having 1 to 22 carbon atom(s) or cycloalkyl having 5 to 12 carbon atoms;

A is a radical of alkylene having 2 to 22 carbon atoms which may be interrupted by nitrogen, oxygen or sulfur;

R_8 is a radical of hydrogen, linear or branched alkyl having 1 to 18 carbon atom(s), a C_4 - C_8 cycloalkyl, such as cyclopentyl, cyclohexyl, phenyl, phenyl which is substituted by 1 or 2

linear or branched alkyl radical(s) together having at most 16 carbon atoms, or is benzyl;
 R_9 is a radical of alkyl having 1 to 18 carbon atom(s);

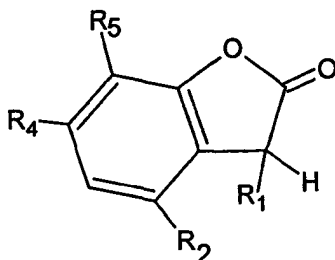
D is -O-; -S-; -SO-; -SO₂- or -C(R₁₁)₂;

the substituents R₁₁, independently of one another, are a radical of hydrogen, C₁-C₁₆ alkyl, the two R₁₁ together containing 1 to 16 carbon atom(s), R₁₁ is furthermore phenyl radical or a radical of the formula

$-(CH_2)_n-CO-O-R_6$ or $-(CH_2)_n-CO-N(R_7)_2$;

in which n, R₆ and R₇ radicals are as defined above;

E is a radical of formula (II)



in which R₁, R₂ and R₄ radicals are as defined above for formula (I); and

R₅ is a radical of hydrogen, linear or branched alkyl having 1 to 20 carbon atom(s), a C₄-C₈ cycloalkyl, such as cyclopentyl, cyclohexyl radical, a halogen atom, such as chlorine, or a radical of the formula

$-(CH_2)_n-CO-O-R_6$ or $-(CH_2)_n-CO-N(R_7)_2$;

in which R₆ and R₇ radicals are as defined above, or R₅ radical together with R₄ radical forms a tetramethylene radical.

Preference is given to those benzofuran-2-ones in which R₃ is a radical of hydrogen, alkyl having 1 to 12 carbon atom(s), cyclopentyl, cyclohexyl, chlorine or a radical of the formula $-(CH_2)_n-CO-O-R_6$; $-(CH_2)_n-CO-N(R_7)_2$ or -D-E,

in which n, R₆, R₇, D and E radicals are as defined above, R₆ is in particular a radical of hydrogen, alkyl having 1 to 18 carbon atom(s), a C₄-C₈ cycloalkyl, such as cyclopentyl or cyclohexyl radical.

Preference is given furthermore to those benzofuran-2-ones in which R₁ is a radical of phenyl or phenyl which is substituted by 1 or 2 linear or branched alkyl radical(s) together having at most 12 carbon atoms; R₂ is hydrogen radical; R₄ is a radical of hydrogen or linear or branched alkyl having 1 to 12 carbon atom(s); R₃ is a radical of hydrogen, linear or branched alkyl having 1 to 12 carbon atom(s), or a radical of the formulae

$-(CH_2)_n-CO-O-R_6$; $-(CH_2)_n-CO-N(R_7)_2$ or $-D-E$;

R_5 is a radical of hydrogen, linear or branched alkyl having 1 to 20 carbon atom(s), or a radical of the formula

$-CH_2-CO-O-R_6$ or $-CH_2-CO-N(R_7)_2$;

or R_5 radical together with R_4 radical forms a tetramethylene radical, n , R_6 , R_7 , D and E radicals being as defined at the beginning

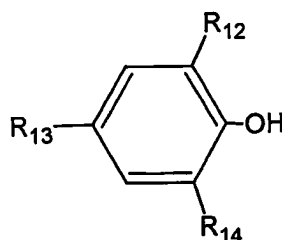
The preferred lactone among the above-mentioned ones is the benzofuran-3-phenyl-2-one type. Such compounds are represented by formula (I) wherein R_1 is a phenyl group and R_2 to R_5 independently is a radical of hydrogen or linear or branched alkyl, preferably hydrogen or C_1 - C_6 alkyl radical.

Further preferred, the lactone comprises 5,7-di-tert-butyl-benzofuran-3-phenyl-2-one, a methyl substituted derivative thereof or a mixture of any of such compounds. Such compounds are represented by formula (I) wherein R_3 and R_5 are tert-butyl radicals, R_2 and R_4 radicals are hydrogen, R_1 is a radical of phenyl which may further be substituted with one or more methyl groups.

In a particular preferred embodiment the lactone comprises a compound selected from the group of 5,7-di-tert-butyl-benzofuran-3-phenyl-2-one, 5,7-di-tert-butyl-benzofuran-3-(3,4-di-methyl-phenyl)-2-one and 5,7-di-tert-butyl-benzofuran-3-(2,3-di-methyl-phenyl)-2-one or a mixture of any of such compounds. Most preferred, the lactone comprises Irganox® HP-136 of Ciba Speciality Chemicals, which is a mixture of the two last mentioned compounds.

Suitable phenolic antioxidants, which generally have a high molecular weight, have general formula:

(III)



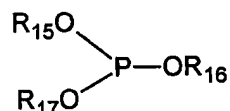
in which R_{12} and R_{14} radicals are equal to or different from each other, and are a radical of linear or branched alkyl group having from 1 to 12 carbon atom(s), and R_3 is a monovalent or polyvalent radical selected from alkyl, aryl, alkylaryl and cycloalkyl groups which can

optionally contain heteroatoms, such as sulphur.

Examples of preferred phenolic antioxidants are: 2,6-dimethyl-3-hydroxy-4-ter-butyl benzyl abietate; tris(4-t-butyl-3-hydroxy-2,6-dimethylbenzyl)-s-triazine-2,4,6-(1H,3H,5H)-trione, which is commercially available from Cyanamid under the Cyanox 1790 trademark; calcium bi[monoethyl(3,5-di-ter-butyl-4-hydroxybenzyl)phosphonate]; 1,3,5-tris (3,5-di-ter-butyl-4-hydroxybenzyl)-s-triazine-2,4,6(1H,3H,5H)-trione; 1,3,5-trimethyl-2,4,6-tris(3,5-di-ter-butyl-4-hydroxybenzyl)benzene; pentaerythritol-tetrakis[3(3,5-di-ter-butyl-4-hydroxyphenyl)propionate], and octadecyl 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate, all of them are commercially available from Ciba Speciality Chemical Corporation under the following trademarks: Irganox 1425, Irganox 3114, Irganox 1330, Irganox 1010, and Irganox1076, respectively.

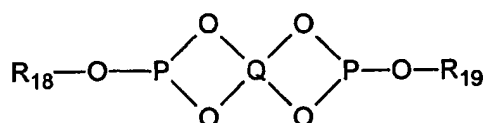
The organic phosphites that can be used as additives for the polyolefins used according to the present invention are preferably selected from general formula

(IV)



in which R_{15} , R_{16} , R_{17} , equal or different, are radicals of alkyl, aryl, or arylalkyl radicals having 1-18 carbon atom(s):

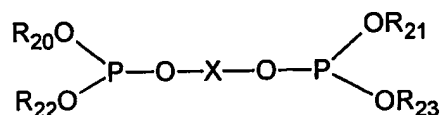
(V)



in which R_{18} and R_{19} , equal or different, are radicals having the above-mentioned meaning for radical R_{15} ;

Q is a tetravalent alkyl radical, such as $\text{C}(\text{CH}_2)_4$;

(VI)



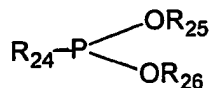
in which R_{20} , R_{21} , R_{22} , R_{23} , equal or different, are radicals having the significance already indicated for radicals R_{15} , X is a bivalent alkyl, aryl, or arylalkyl radical.

Examples of organic phosphites comprised in general formula IV are described in US Patents No. 4,187,212 and No. 4,290,941, which are incorporated herein for reference.

Specific examples of compounds included in general formulas IV, V, VI are: tris(2,4-di-ter-butylphenyl)phosphite commercially available from Ciba Speciality Chemicals Corporation under the Irgafos 168 trademark; distearyl pentaerythritol diphosphite commercially available from Borg-Warner Chemical under the Weston 618 trademark; 4,4'-butylidenebis(3-methyl-6-ter-butylphenyl-ditridecyl)phosphite commercially available from Adeka Argus Chemical under the Mark P trademark; tris(monononylphenyl)phosphite; bis(2,4-di-ter-butyl)pentaerythritol diphosphite, commercially available from Borg-Warner Chemical under the Ultrinox 626 trademark.

The organic phosphonites that can be used as additives according to the present invention are preferably selected among the compounds of general formula:

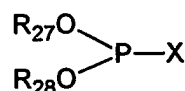
(VII)



in which R_{24} , R_{25} , R_{26} , equal or different, are alkyl, aryl, or arylalkyl radicals having 1-18 carbon atom(s).

Alternatively, and this is preferred, the R_{24} radical can be substituted by a group

(VIII)



in which R_{23} and R_{24} , equal or different, are radicals having the above indicated significance for the R_{20} radicals, and X is a bivalent alkyl, aryl, or arylalkyl radical.

Examples of organic phosphonites included in general formula VII, which can conveniently be used according to the present invention, are described in GB patent No. 1,372,528.

A preferred example of compounds comprised in general formula VII is the tetrakis(2,4-di-ter-butylphenyl)4,4'-diphenylenediphosphonite, commercially available from Sandoz under the Sandostab P-EPQ trademark.

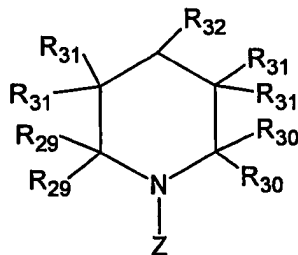
The organic phosphites and phosphonites are generally used to inhibit degradation and oxidation of polyolefins in the molten state (process stabilizers), and therefore, according to the state of the art, require the addition of high quantities of phenolic stabilizers to obtain a complete stabilization.

The HALS, which according to the present invention are also used as polyolefins stabilisers, are amine compounds with steric hindrance of the aminic function, which are generally used as stabilisers for polyolefins in the solid state against oxidation induced by light.

In the said case as well, according to the state of the art, the addition of a high quantity of phenolic stabilisers is necessary for a satisfactory stabilization of polyolefin manufactured articles.

The HALS used according to the present invention are monomeric or oligomeric compounds containing, in the molecule, one or more substituted piperidine groups having general formula:

(IX)



in which the R_{29} radicals, equal or different, are C_1 - C_4 alkyl radicals, or tetramethylpiperidine radicals, or the alkyl radicals form with the piperidine carbon atoms to which they are linked a C_5 - C_9 cycloalkyl radical; the R_{30} radicals, equal or different, are hydrogen or C_1 - C_{18} alkyl radicals, C_7 - C_{18} arylalkyl radicals, or the alkyl radical forms with the piperidine carbon atoms to which they are linked a C_5 - C_{10} cycloalkyl radical; the R_{31} radicals, equal or different, are hydrogen, or C_1 - C_{18} alkyl radicals or C_7 - C_{18} arylalkyl radicals; the R_{32} radical is hydrogen, or a C_1 - C_8 alkyl radical, or a benzyl radical; Z is hydrogen, or a C_1 - C_{18} alkyl, C_1 - C_{12} alkylene, C_3 - C_{12} alkenyl, C_3 - C_5 alkynyl, C_7 - C_{18} arylalkyl, C_2 - C_4 acyl, C_2 - C_{18} alkanoyl, C_3 - C_{18} alkoxyalkyl, C_3 - C_{18} alkenoyl, oxylic, cyanomethyl, xylylenyl radical, or a radical having a 1 to 4 valence and containing from 1 to 4 hydroxyl groups and, optionally, ether, ester, or heterocyclic groups, being the valences of said radical linked to the nitrogen of piperidine groups, or a bivalent radical containing one or more ester or amide groups, or a $-CO-N(R_{33})(R_{34})$ radical where R_{33} and R_{34} are hydrocarbon radicals.

Preferably Z is a C₁-C₁₂ alkyl radical, or a C₃-C₈ alkenyl, C₇-C₁₁ aralkyl radical, or a bivalent radical containing one or more ester groups, being the valences of said radicals linked to the nitrogen atom of piperidine groups.

Specific examples of preferred HALS according to the present invention include poly[[6-[(1,1,3,3-tetramethylbutyl)amino]-1,3,5-triazine-2,4-diyl][(2,2,6,6-tetramethyl-4-piperidiny)imino]-1,6-hexanediy[(2,2,6,6-tetramethyl-4-piperidiny)imino]]; N,N',N'',N'''-tetrakis(4,6-bis(butyl-(N-methyl-2,2,6,6-tetramethylpiperidin-4-yl)-amino)triazin-2-yl)-4,7-diazadecane-1,10-diamine; (1,6-hexanediamine, N, N'-bis(2,2,6,6-tetramethyl-4-piperidiny)-polymer, and poly-(N-β-hydroxyethyl-2,2,6,6-tetramethyl-4-hydroxy-piperidyl succinate). They are commercially available from Ciba Speciality Chemicals Corporation under the Chimassorb 944 trademark, Chimassorb 119 trademark, Chimassorb 2020 trademark and Tinuvin 622 trademark, respectively.

The olefin polymer can be polyethylene, such as HDPE, LLDPE, LDPE, or preferably a crystalline propylene polymer, most preferably either a crystalline propylene homopolymer having a moiety soluble in xylene at ambient temperature greater than 90, most preferably greater than 93, or a semi-crystalline, random polymer of propylene and ethylene and/or linear or branched C₄-C₁₀ α-olefin with a moiety soluble in xylene at ambient temperature greater than 85, or their mixtures. The preferred α-olefins are 1-butene, 1-hexene, 1-octene, 4-methyl-1-pentene. In the polymer the total comonomer content varies from 0.05% to 20% by weight. The above-mentioned crystalline polymers preferably have a stereoregularity of isotactic type of the propylenic sequences.

Heterophasic olefin polymer compositions can also be used and are constituted by (A) crystalline olefin polymer as mentioned above, and (B) an elastomeric olefin polymer. The composition typically contains polymer fraction (B) in quantities from 5% to 80% by weight, and crystalline polymer (A) in quantities from 20% to 95% by weight. The elastomeric olefin polymer is typically a polymer of ethylene with a C₃-C₁₀ α-olefin and optionally a diene, wherein the ethylene content typically ranges from 15 to 85% by weight and, when present, the diene content ranges from 0.5 to 5% by weight. Polymer (B) is preferably selected from ethylene-propylene copolymer and ethylene-propylene-diene rubber terpolymer. Said heterophasic polymer compositions are prepared according to known methods via mixing in the melted state of the above-mentioned components, or sequential copolymerization in the presence of stereospecific catalysts, such as Ziegler-Natta catalysts.

The crystalline propylene polymer can also have stereoregularity of syndiotactic type of the propylenic sequences

In general, the additivated polyolefins used to prepare the fibres according to the present invention have a melt flow index value, determined according to method hereinbelow, between 0.5 and 100 g/10 minutes, more preferably between 1.5 and 35 g/10 minutes, obtained directly in polymerization or through controlled radical degradation.

The stabiliser mixture components may be incorporated into the olefin polymer in any conventional methods, such as by dry blending the stabilisers directly with polymer pellets, by means of tumble mixers and Henschel blenders. Solutions, emulsions or slurries of the stabiliser mixture components can be sprayed onto or admixed with granular polymers, with or without subsequent evaporation of the solvent. For example, granules of the olefin polymer can be coated or impregnated with the stabiliser components in a fluidised bed according to the process of U.S. Patent No. 5,141,772. The stabiliser components can also be blended with molten polymers by means of a Banbury mixer, Brabender mixer, roll mill or screw extruder.

The stabiliser mixture components can also be added to the olefin polymer in the form of a masterbatch according to the conventional techniques discussed in U.S. Patent No. 5,236,962.

In addition to the above-mentioned stabiliser mixture, the olefin polymer of the present invention may contain other additives as appropriate for the intended use of the polymer composition, i.e. fibres, provided that the added additives are not stabilisers. Suitable further additives commonly employed in the art are anti-slip agents, antistatic agents, flame retardants, fillers, nucleating agents, pigments, anti-soiling agents, photosensitizers, for example.

In another aspect, the present invention is directed to thermoweldable fibres made up of olefin polymers containing the stabilisers in the above-mentioned amounts. More particularly, it relates to staple fibres.

Typically, the fibres according to the present invention have tenacity of at least 16 cN/tex and/or elongation at break of at least 200% and/or bonding force at 150° C of at least 350 cN.

Typically, the fibres according to the present invention have a titre ranging from 1.5 to 2.5 dtex.

The fibres of the present invention can be prepared by way of any melt spin process known in the art. In particular, they can be prepared in form of staple fibres, by using both long-spinning and short-spinning apparatuses.

The long-spinning apparatuses normally comprise a first spinning section where the fibres are extruded and air-cooled in a quenching column at a relatively high spinning speed. Subsequently, these fibres go to the finishing step, during which they are drawn, crimped-bulked and cut. Generally, the above mentioned finishing step is carried out separately with respect to the spinning, in a specific section where the fibre rovings are gathered into one single big roving. Said big roving is then sent to drawing, crimping-bulking and cutting apparatuses which operate at a speed ranging from 100 to 200 m/min.

In other types of long-spinning apparatuses the above mentioned finishing steps are carried out in sequence with the spinning step. In this case the fibres go directly from the gathering to the drawing rollers, where they are drawn.

The process conditions generally adopted when using the long-spinning apparatuses are the following:

- output per hole: greater than 0.1 g/min, preferably from 0.15 to 1 g/min, more preferably from 0.2 to 0.5 g/min;
- take up speed: equal to or higher than 500 m/min, preferably from 500 to 3500 m/min, more preferably from 600 to 2000 m/min;
- space where the fibres cool off and solidify after exiting the die: greater than 0.50 m.

Moreover, it is preferable that the draw ratio be from 1.1 to 4.

For further details on the long-spinning apparatuses reference is made to Friedelm Hauser "Plastics Extrusion Technology", Hauser Publishers, 1988, chapter 17.

The short-spinning apparatuses allow for a continuous operation, since the spinning speed is compatible with the drawing, crimping and cutting speeds.

The process conditions which are best suited to be used according to the present invention using short-spinning apparatuses are the following. The output per hole ranges from 0.005 to 0.18 g/min, preferably from 0.008 to 0.07 g/min, more preferably from 0.01 to 0.03 g/min. The take up speed ranges from 30 to 500 m/min, preferably from 40 to 250 m/min, more preferably from 50 to 100 m/min. The draw ratios range from 1.1 to 3.5, preferably from 1.2 to 2.5. Moreover, the fibre cooling and solidification space at the output of the die (cooling space) is preferably greater than 2 mm, more preferably greater than 10 mm, in particular

from 10 to 350 mm. Said cooling is generally induced by an air jet or flow.

For further details on the short-spinning apparatuses reference is made to M. Ahmed, "Polypropylene fibres science and technology", Elsevier Scientific Publishing Company (1982) pages 344-346.

The spinning temperature for the above long-spinning and short-spinning apparatuses generally ranges from 220° to 340° C, preferably from 250° to 300° C. In particular, the extruding temperature can range from 260° to 275° C without negatively affecting the capability of the fibre to bond each other.

After the production of the staple in a first step, there is the formation of a fibre web by passing the staple fibres through a carding machine, and by thermal bonding by calendering (calender rolls are employed).

Independently from the specific thermal bonding method employed, the bonding temperatures are preferably within the range from 120° to 160° C, more preferably from 130° to 145° C.

A further embodiment of the present invention relates to thermally bonded articles, in particular non-woven fabrics, produced with the staple fibres according to the present invention.

In a further embodiment, the present invention relates to a multilayer non-woven fabric made from two or more layers wherein at least one layer is made of the above-mentioned thermal-bonded non-woven fabric. The other layer(s) may be non-woven fabric(s) as well that is/are made of other kind of polymers or polymer compositions.

The non-woven fabric according to the present invention may also be laminated with cast film for producing another type of composite structure.

Typically, a non-woven fabric with a weight of 20 grams/m² made according to the present invention has CD tenacity of at least 8 N/5cm and/or MD tenacity of at least 30 N/5cm and CD elongation at break of at least 35% and/or MD elongation at break of at least 30%. It typically has a value of thermal-bonding index of at least 15 N/5cm.

The abbreviation "MD" means "machine direction", and refers to a direction "along the length" of the fibre, i.e., in the direction of the fibre; the abbreviation "CD" means "cross direction", and refers to a direction across the fibre, perpendicular to the machine or longitudinal direction.

The following examples are given to illustrate and not to limit the present invention.

The data relating to the polymer and the fibres of the examples are determined by way of the methods reported below.

- MFR: according to the ISO method 1133 (230° C, 2.16 kg).
- Titre of fibres: from a 10 cm long roving, 50 fibres are randomly chosen and weighed. The total weight of the said 50 fibres, expressed in mg, is multiplied by 2, thereby obtaining the titre in dtex.
- Tenacity and Elongation (at break) of fibres: from a 500 m roving a 100 mm long segment is cut. From this segment the single fibres to be tested are randomly chosen. Each single fibre to be tested is fixed to the clamps of an Instron dynamometer (model 1122) and tensioned to break with a traction speed of 20 mm/min for elongations lower than 100% and 50 mm/min for elongations greater than 100%, the initial distance between the clamps being of 20 mm. The ultimate strength (load at break) and the elongation at break are determined.

The Tenacity is derived using the following equation:

$$\text{Tenacity} = \text{Ultimate strength (cN)} \times 10 / \text{Titre (dtex)}.$$

- Bonding force of fibres: specimens are prepared from a 400 tex roving (method ASTM D 1577-7) 0.4 meter long, made up of continuous fibres. After the roving has been twisted eighty times, the two extremities are united, thus obtaining a product where the two halves of the roving are entwined as in a rope. The thermal bonding is carried out on said specimen using a Bruggel HSC-ETK thermal bonding machine, operating at various plate temperatures (see in the tables) using a clamping pressure of 0.28 MPa and 1 second bonding time. The previously said dynamometer, operated at a traction speed of 2 cm/min, is used to measure the average force required to separate the two halves of the roving which constitute each specimen at the thermal bonding point. The obtained graph shows the force varying from minimum to maximum values (peaks are obtained). The value resulting from averaging out all the minimum and maximum values shown in the graph represents the said average force. The result, expressed in cN, is obtained by averaging out at least eight measurements, and represents the bond strength of the fibres. When non-woven samples are prepared, the bond strength is determined on specimens 20 cm long and 5 cm wide. The 5 cm wide extremities are fixed to the clamps of the dynamometer and tensioned at a clamp speed of 100 mm/min (the initial distance between the clamps being of 10 cm). The maximum force measured in the machine direction (MD)

and in the cross direction (CD), with respect to the calendering step, represents the strength of the fibres.

- Thermal Bonding Index: calculated as $\sqrt{(Ten_{CD} \times Ten_{MD})} \times 20/X$, wherein X is the weight of the non-woven fabric, and 20 is the reference weight.

Example 1

In a twin-screw extruder a propylene homopolymer (MFR 11 g/10 min and solubility in xylene at room temperature of 3.2% by weight) is mixed, molten and granulated in the presence of 200 ppm of calcium stearate as anti acid agent and a stabiliser composition consisting of:

- 125 ppm of a octadecyl 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate, marketed with the trademark Irganox 1076 by Ciba Speciality Chemical Corporation,
- 110 ppm of 5,7-di-tert-butyl-3-(3,4-di-methylphenyl)-3H-benzofurane-2-one, marketed with trademark Irganox HP136 by Ciba Speciality Chemical Corporation,
- 220 ppm of tris(2,4-di-tert-butylphenyl)phosphite, marketed with the trademark Irgafos 168 by Ciba Speciality Chemical Corporation, and
- 200 ppm of poly(N-β-hydroxymethyl-2,2,6,6-tetramethyl-4-hydroxy-piperidyl succinate), marketed with the trademark Tinuvin 622 by Ciba Speciality Chemical Corporation).

The stabilised polymer is spun in a conventional long spinning line operating at conditions reported in Table 1. The filament is online stretched and crimped. The stretching conditions are reported in Table 2.

The 40 mm staple fibres thus obtained have the mechanical features and spinning behaviour reported in Table 3.

Table 1

Spinnerette temperature, ° C	290
Melting temperature, ° C	287
Quenching air temperature, ° C	12-14
Throughput, g/min×hole	0.345

Table 2

1 st godet speed, r.p.m.	1510
1 st godet temperature, ° C	40
2 nd godet speed, r.p.m.	1520
2 nd godet temperature, ° C	40
3 rd godet speed, r.p.m.	1920
3 rd godet temperature, ° C	120
4 th godet speed, r.p.m.	1900
4 th godet temperature, ° C	115
4 th godet speed/1 st godet speed ratio	1.26

Table 3

Properties of 40 mm Staple Fibres	Example 1	Comparative example 1
Average filament titer, dtex	2.16	2.12
MFR, g/10'	38	65
Tenacity, cN/tex	19.8	15.3
Elongation at break, %	325	225
Spinning behaviour	Good	Poor ¹⁾

¹⁾ Breakage of several filament during the spinning.

Comparative Example 1

Example 1 is repeated with the only difference that the stabiliser composition is phenol-free.

The staple fibres obtained have the mechanical features and spinning behaviour listed in Table 3.

The fibres of example 1 have much more tenacity and elongation than the ones of comparative example 1, the latter being affected by evident polymer degradation.

Example 2

The staple fibres produced in example 1 are carded/calendered using a conventional carding/calendering machine using the conditions reported in Table 4 to produce a non-woven fabric having a 20g/m² weight.

Table 4

Carding speed, m/min	120
Embossed calendering roll temperature, ° C	150
Smooth calendering roll temperature, ° C	139

Comparative Example 2

The staple fibres produced in comparative example 1 are carded/calendered using the same conventional carding/calendaring machine and the same setting conditions used for the example 1.

Table 5 contains the properties of the non-woven fabric produced in example 2 and comparative example 2, respectively.

The Edana Standard Method is used to test the properties of the non-woven fabric.

Table 5

Properties of the Non-Woven Fabric	Comparative example 2	Example 2
Weight, g/m ²	20	20
CD Tenacity, N/5cm	4.2	12.0
MD Tenacity, N/5cm	25.0	37.0
CD Elongation at break, %	32	42
MD Elongation at break, %	28	35
Thermal Bonding Index, N/5cm	11.6	21.1

In Table 5 some properties of the non-woven fabric are reported. In particular, the thermal bonding index and tenacity of the non-woven fabric according to the present invention are remarkably improved. The thermal bonding index is almost twice the one of the comparison fabric and CD tenacity is almost 3 times the CD tenacity of the comparison fabric.

Although the phenolic antioxidant is present, both the fibres of example 1 and the nonwoven fabric of example 2 show no colour change (gas fading).

Example 3 and Comparative Example 3

The compositions obtained in example 1 and comparative example 1 are spun in a Leonard 25 spinning pilot line having length/diameter ratio of the screw of 25, screw diameter of 25 mm and compression ratio of 1:3. The line is marketed by Costruzioni Meccaniche Leonard-Sumirago (VA).

Spinning tests are carried out with the following conditions: hole diameter: 0.4 mm, output: 0.4 g/min×hole and mechanical values are measured at 1500 m/min winding speed with stretching ratio 1:1.5.

The properties of the fibres thus obtained are reported in Table 6.

In Table 6 the data show that with respect to the comparative one, the polymer composition according to the present invention is easily and steadily processable and at the same time the fibres obtained have good values of the tenacity and particularly bonding force, while it is not even possible to process the polymer composition of comparative example due to a severe melt degradation, resulting in insufficient melt strength and thus not stable spinning process. Related fibres can not be collected for testing.

Table 6

Process Conditions and Properties of Fibres	Example 3	Comparative example 3
Extrusion temperature, °C	280	280
MFR, g/10 min	70	polymer drops out of the spinneret spinning not stable
Fibre titre, dtex	2.0	-
Tenacity, cN/tex	25.4	-
Elongation at break, %	235	-
Bonding force at 150° C, cN	645	-
Bonding force at 145° C, cN	420	-

Examples 4 and 5

The compositions of example 1 are spun in a Leonard 25 spinning pilot line having length/diameter ratio of the screw of 5 and marketed by Costruzioni Meccaniche Leonard-Sumirago (VA).

The spinning conditions are the same as the ones of example 3 except for lower extrusion temperatures as reported in Table 8.

The properties of the fibres thus obtained are reported in Table 7.

Comparative Examples 4 and 5

Examples 4 and 5 are repeated except that the composition of comparative example 1 is used in the place of that of example 1.

Table 7

Process Conditions and Properties of Fibres	Examples		Comparative Examples	
	4	5	4	5
Extrusion temperature, °C	270	265	270	265
MFR, g/10 min	45	25	polymer drops out of the spinneret spinning not stable	polymer drops out of the spinneret spinning not stable
Fibre titre, dtex	2.0	2.0	-	-
Tenacity, cN/tex	23.9	24.7	-	-
Elongation at break, %	275	275	-	-
Bonding force at 150° C, cN	780	370	-	-

In Table 7 the data show that with respect to the comparative ones, the polymer composition according to the present invention is easily processable and the fibres obtained maintain a good bonding force value even at lower MFR of the fibre achieved at lower extrusion temperature. In contrast, the comparative polymer is not processable in spite of a lower extrusion temperature that should increase the melt strength, and is subjected to chemical degradation.

The compositions according to the present invention allow to obtain fibres that have high bonding force values because of low polymer degradation and show good balance between tenacity and elongation in a wide range of extrusion temperatures (265 – 280° C).

Example 6

The composition of example 1 is subjected to a test of multiple extrusion process. MFR values are measured on the polymer before extrusion and then after a 3rd and 5th re-granulation passage in a COMACPLAST 19 extruder. The operating profile of the extrusion process is as follows:

- Melt temperature: 287° C,
- Head pressure: 1.9×10^{-4} Pa,
- Screw speed: 150 rpm.

Comparative Example 6

Example 6 is repeated with the exception that the composition of comparative example 1 is used in the place of that of example 1.

The good melt retention of stabiliser mixture components according to the present invention is confirmed by a multiple extrusion test.

Table 8

MFR and MFR variation	Example 6	Comparative Example 6
MFR before the first passage (MFR 1 st), g/10 min	12.6	9.3
MFR after the 3 rd passage (MFR 3 rd), g/10 min	30.7	37.3
MFR variation after the third passage, %	144	300
MFR after the 5 th passage (MFR 5 th), g/10 min	60	81.4
MFR variation after the fifth passage, %	375	775

$$\text{MFR variation at the 3}^{\text{rd}} \text{ passage} = \frac{\text{MFR}_{3\text{rd}} - \text{MFR}_{1\text{st}}}{\text{MFR}_{1\text{st}}} \times 100;$$

$$\text{MFR variation at the 5}^{\text{th}} \text{ passage} = \frac{\text{MFR}_{5\text{th}} - \text{MFR}_{1\text{st}}}{\text{MFR}_{1\text{st}}} \times 100.$$

In Table 8 the data show that the polymer composition according to the present invention has a better melt stability than that of comparative example 1 as shown by a lower increase of the MFR value after the multiple extrusion passages.

CLAIMS

1. An olefin polymer composition comprising (ppm with respect to the polymer):
 - a lactone of the furan-2-one type,
 - a phenol in amounts of 50 to 200 ppm,
 - a sterically hindered amine in amounts of 50 to 300 ppm, and
 - an organic phosphite and/or organic phosphonite in amounts of 50 to less than 280 ppm;the polymer composition containing the unsubstituted furan-2-one moiety in amounts ranging from 11 to 49 ppm with respect to the polymer.
2. The olefin polymer composition according to claim 1, wherein the polymer composition contains 40 to 220 ppm of lactone of the furan-2-one type.
3. The olefin polymer composition according to claim 1, wherein the lactone is selected from 5,7-di-tert-butyl-benzofuran-3-phenyl-2-one, 5,7-di-tert-butyl-benzofuran-3-(3,4-di-methyl-phenyl)-2-one and 5,7-di-tert-butyl-benzofuran-3-(2,3-di-methyl-phenyl)-2-one or a mixture of any of such compounds.
4. The olefin polymer composition according to claims 1 to 3 wherein the olefin polymer is selected from:
 - 1) isotactic homopolymer of propylene;
 - 2) polyethylene;
 - 3) crystalline polymers of propylene with ethylene and/or other linear or branched C₄-C₁₀ α -olefins, where the total comonomer content varies from 0.05% to 20% by weight; and
 - 4) heterophasic olefin polymer composition constituted by (A) crystalline polymer selected from an isotactic homopolymer of propylene or one of the polymers mentioned in item (3), and (B) an elastomeric olefin polymer.
5. A process for preparing the olefin composition according to claims 1 to 4 wherein the stabiliser components according to claim 1 are incorporated into the olefin polymer.
6. Thermoweldable fibres made up of the olefin polymer composition according to claims 1 to 4.
7. The thermoweldable fibres according to claim 6 wherein the fibres are staple fibres.
8. A process for producing fibres according to claims 6 and 7 which comprises spinning fibres from the olefin polymer composition according to claims 1 to 4 in the molten state

and drawing the solid fibres.

9. Non-woven fabric produced from the thermoweldable fibres according to claims 6 and 7.
10. Multilayer non-woven fabric produced from the thermoweldable fibres according to claims 6 and 7.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 2004/006542

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08K5/1535 C08K5/00 D01F1/10 D01F6/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08K D01F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	GB 2 322 374 A (CIBA SC HOLDING AG) 26 August 1998 (1998-08-26) cited in the application page 67, paragraph 3-6; claims 1-29 page 78, paragraph 7 tables 1,2	1-10
Y	US 5 834 541 A (STARSINIC MICHAEL E ET AL) 10 November 1998 (1998-11-10). cited in the application claims 11,19,20 column 9, line 15 - column 14, line 55 ----- -/-	1-10

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

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O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

G document member of the same patent family

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 2004/006542

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 1 260 618 A (BOREALIS TECH OY) 27 November 2002 (2002-11-27) cited in the application claims 1-11,18,23-25 paragraphs '0001! - '0008!, '0013!, '0014!, '0038! - '0046!; example all	1-10
A	KRÖHNKE C.: "A major breakthrough in polymer stabilisation" 1997, POLYOLEFINS X INTERNATIONAL PROCEEDINGS , XPO09036220 the whole document	1-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 2004/006542

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
GB 2322374	A	26-08-1998	BE 1011643 A3	09-11-1999
			DE 19806846 A1	27-08-1998
			ES 2138926 A1	16-01-2000
			FR 2760005 A1	28-08-1998
			IT MI980307 A1	18-08-1999
			JP 10236988 A	08-09-1998
			NL 1008373 C2	19-04-1999
			NL 1008373 A1	24-08-1998
US 5834541	A	10-11-1998	AT 249493 T	15-09-2003
			AU 733943 B2	31-05-2001
			AU 6378298 A	05-11-1998
			BR 9801528 A	29-06-1999
			CA 2236634 A1	02-11-1998
			CN 1198448 A	11-11-1998
			CZ 9801330 A3	11-11-1998
			DE 69817906 D1	16-10-2003
			DE 69817906 T2	22-07-2004
			EP 0875530 A1	04-11-1998
			HU 9800914 A2	30-11-1998
			JP 10306178 A	17-11-1998
			NO 981917 A	03-11-1998
			PL 326099 A1	09-11-1998
			SK 48498 A3	04-11-1998
			TW 401441 B	11-08-2000
EP 1260618	A	27-11-2002	EP 1260618 A1	27-11-2002
			WO 02095095 A2	28-11-2002